



PERSONAL COOLING FABRIC BASED ON POLYMERIC THERMOELECTRICS

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July 2016

Final Report
April 2009 – February 2012

Approved for public release; distribution is unlimited

**U.S. Army Natick Soldier Research, Development and Engineering Center
Natick, Massachusetts 01760-5020**

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REPORT DOCUMENTATION PAGE					Form Approved OMB No. 0704-0188																									
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1. REPORT DATE (DD-MM-YYYY) 28-07-2016		2. REPORT TYPE Final		3. DATES COVERED (From - To) April 2009 – February 2012																										
PERSONAL COOLING FABRIC BASED ON POLYMERIC THERMOELECTRICS				5a. CONTRACT NUMBER																										
				5b. GRANT NUMBER																										
				5c. PROGRAM ELEMENT NUMBER																										
6. AUTHOR(S) Eugene Wilusz, Frank E. Karasz*, Patrick S. Taylor*, Ljiljana Korugic-Karasz*, and Paul M. Lahti**				5d. PROJECT NUMBER BA08PRO017																										
				5e. TASK NUMBER																										
				5f. WORK UNIT NUMBER																										
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Natick Soldier Research, Development and Engineering Center ATTN: RDNS-SEW-TMC 10 General Greene Avenue, Natick, MA 01760-5020				8. PERFORMING ORGANIZATION REPORT NUMBER																										
				NATICK/TR-16/018																										
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Defense Threat Reduction Agency 8275 John J. Kingman Rd. Stop 6201 Fort Belvoir, VA 22060-6201				10. SPONSOR/MONITOR'S ACRONYM(S) DTRA																										
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)																										
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited																														
13. SUPPLEMENTARY NOTES * University of Massachusetts, Department of Polymer Science and Engineering, Amherst, MA 01002 ** University of Massachusetts, Department of Chemistry, Amherst, MA 01002																														
14. ABSTRACT This report documents a 3-year effort (completed in 2012) sponsored by the Defense Threat Reduction Agency (DTRA) to develop novel polymeric thermoelectric (TE) materials, to develop an understanding of the TE behavior of these materials, and to provide materials from which a personal cooling fabric could be developed. Organic polymers offer a light weight, environmentally friendly, and low cost alternative to the widely used inorganic TE materials. Because of their potential for good electrical conductivity and the discrete nature of their conjugated blocks, a series of poly(phenylenevinylene) (PPV) copolymers was chosen for this work. The TE Figure of Merit for films of these copolymers was found to vary over a wide range. The most promising results were obtained by blending single wall carbon nanotubes into the polymers to increase electrical conductivity. The highest value obtained for the Figure of Merit was approximately 0.01, among the highest observed for any organic thermoelectric materials. Further materials development can be expected to yield second generation TE polymers with improved properties.																														
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a. REPORT	b. ABSTRACT	c. THIS PAGE			Eugene Wilusz																									
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Preface

This final report documents the efforts and results of a Natick Soldier Research, Development and Engineering Center (NSRDEC) project, conducted between April 2009 and February 2012, to develop materials for use in a personal cooling fabric based on polymeric thermoelectrics. This effort was sponsored by the Defense Threat Reduction Agency under project number BA08PRO017, and the majority of the work was performed by the University of Massachusetts Amherst under a grant issued by NSRDEC.

PERSONAL COOLING FABRIC BASED ON POLYMERIC THERMOELECTRICS

1. INTRODUCTION

This report documents a 3-year collaborative effort (completed in 2012) between the Natick Soldier Research, Development and Engineering Center (NSRDEC) and the University of Massachusetts Amherst (UMass) to extend research begun over two decades ago to develop novel thermoelectric (TE) materials for use in a personal cooling fabric based on conductive polymeric or low molecular weight organic materials as a light weight, environmentally friendly, and low cost alternative to the widely used inorganic TE materials. This work was conducted under an NSRDEC project sponsored by the Defense Threat Reduction Agency. The focus of this work was on a series of poly(phenylenevinylene) (PPV) copolymers because of the potential for good electrical conductivity demonstrated in previous research efforts and the discrete nature of the copolymers' conjugated blocks.

TE technology presents major opportunities in the areas of power generation and thermal energy transfer¹⁻⁴. TE technologies are fundamental to solid state cooling and power generation systems in a wide range of capacities from electronic devices to air conditioning modules to power modules on deep space probes⁵. TE materials have been widely used in the areas of electric power generation (Seebeck effect) and as active cooling components (Peltier effect) in the industrial and electronics industries for the last half century, and numerous applications to both military and civilian technologies have emerged. The military, avionic, and auto industries can utilize this technology to capture waste engine heat, reducing the need for additional electric power generators, and improve the overall performance of the vehicles. The clothing industry, for both military and civilian personnel, could exploit the properties of the Peltier effect in TE materials to develop lightweight heating or cooling fabrics. This would alleviate the need for 1) bulky, heavy insulating materials used in extremely cold environments, providing increased mobility, and 2) a means to eliminate heat-related ailments typically encountered in the dry, arid environment of deserts.

Developing new materials with enhanced TE capabilities for application in these areas involves scientific and technological challenges, and there has been considerable research worldwide in this area over the last 40 years⁶⁻⁸. To be considered practical, thermoelectric materials need to have the dimensionless figure of merit ($ZT \geq 1$) (Eq. 1),

$$ZT = S^2 \sigma T / \kappa \quad (\text{Eq. 1})$$

where S is the Seebeck coefficient ($\mu\text{V/K}$), σ is the electrical conductivity (S/cm), κ is the thermal conductivity ($\mu\text{W/m}^2\text{K}$), and T is the absolute temperature (K).

When the thermal conductivity of the substance is unknown or assumed to be similar to the class of materials under investigation, TE performance is described by the power factor (Eq. 2).

$$\text{PF} = S^2 \sigma \quad (\text{Eq. 2})$$

Most inorganic TE materials based on skutterudites, clathrates, and pentatellurides have ZTs considerably lower than 1 and have showed little improvement in performance over the last 40 years. Bismuth telluride alloys have been widely developed, are the most common of the inorganic materials used, and show the best TE performance of all materials studied.⁷ However, these metallic materials are not competitive in terms of efficiency or weight and cannot be easily incorporated into large-scale fabric platforms, resulting in high-cost systems. There are also concerns about environmental impact given their toxic heavy metal content.

Despite these limitations and the lack of improvement in the inorganic materials, an extremely small portion of the TE research efforts over the past 40 years has been directed to polymeric or low molecular weight organic materials. Furthermore, p- and n-doped conjugated polymers with high electrical conductivity were discovered over two decades ago, suggesting that investigation of the properties of these materials would be profitable. In all of the relatively few studies where appropriate polymeric TE materials were studied, they offered the additional advantages (over metallic materials) of low density, no toxic heavy metals (bismuth, lead, mercury, etc.), and an essentially unlimited material supply at low to moderate cost. The objective of that relatively limited work has been to develop and study the TE behavior of novel polymeric materials so they can be used to develop a personal cooling fabric. Such a fabric could provide numerous advantages that can be readily realized: absence of moving parts, light weight, environmentally friendly construction (no chlorofluorocarbon or other gases), and low cost. Identification and development of the needed materials requires both a materials and textile engineering study.

Conductive polymers became attractive candidates due to their versatile chemical structures, low cost, ease of incorporation onto a variety of platforms, and presumed low thermal conductivity^{9, 10}. The potential high ZT of these materials contributed to the desirability of finding structures to tune the conductivity of the materials without significantly altering their TE properties or their thermal conductivities. Recently, selective tuning of the conductivity of (poly(3,4-ethylene dioxythiophene) p-toluenesulfonic acid (PEDOT:p-TSA) has shown a ZT as high as 0.25 at room temperature¹¹. Polymer blends and composites have also been used to alter the electronic properties of polymer systems to modulate the TE performance of the materials¹²⁻¹⁷.

Using a variety of poly(phenylenevinylene) (PPV) polymers, Toshima, et al have shown that upon orientation they were able to increase the conductivity of their doped films by almost three orders of magnitude with very little change in Seebeck coefficient and thermal conductivity, providing materials with ZT ~0.1 at room temperature^{18, 19}. Casian, et al performed a detailed theoretical analysis of the TE behavior of tetrathiafulvalene-tetracyanoquinodimethane (TTF:TCNQ) and found there could be a simultaneous increase in both the Seebeck coefficient and the electrical conductivity²⁰⁻²³. This hypothesis was based on analysis of the discrete packing pattern of the TTF:TCNQ radical ion pairs.

2. METHODOLOGY

Using the general concept used by Casian, et al, the NSRDEC/UMass team investigated the TE properties of a series of PPV copolymers (Figure 1): Poly(1,8-octanedioxy-2,6-dimethoxy-1,4-phenylene-1,2-ethynylene-1,4-phenylene-1,2-ethynylene-3,5-dimethoxy-1,4-phenylene) (2.5 PPV-Octyl), Poly(1,2-ethanedioxy-2,6-dimethoxy-1,4-phenylene-1,2-ethynylene-1,4-phenylene-1,2-ethynylene-3,5-dimethoxy-1,4-phenylene) (2.5 PPV-Et), and Poly(1,4-butanedioxy-1,4-phenylene-1,4-butanedioxy-2,6-dimethoxy-1,4-phenylene-1,2-ethynylene-1,4-phenylene-1,2-ethynylene-3,5-dimethoxy-1,4-phenylene) (2.5 PPV-BuPhBu). It was postulated that the discrete nature of the conjugated blocks provide a similar structural motif to that of TTF:TCNQ packing and would allow for simultaneous increase in Seebeck coefficient and conductivity, thus yielding a variety of conductive polymers with enhanced TE properties. The electrical conductivity and TE properties of TTF-TCNQ, an n-type conductive salt, dispersed in 2.5 PPV-Octyl were also chosen for investigation, as was the existence of the Peltier effect of all the samples studied.

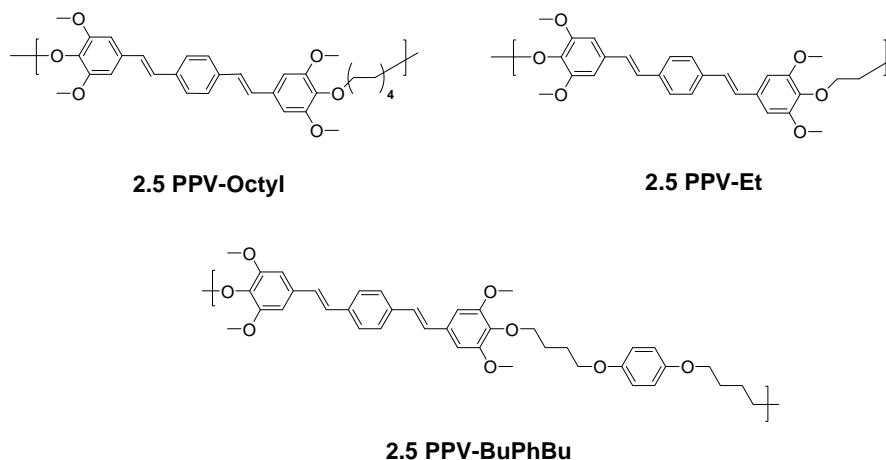


Figure 1. 2.5 PPV Copolymers Investigated

The electro- and photo-luminescent properties of the 2.5 PPV-Octyl and 2.5 PPV-Et copolymers were previously studied by Karasz and coworkers²⁴⁻²⁷. Electrical conductivities of structurally similar 2.5 PPV ether and ester derivatives doped with I₂ under ambient conditions were of the order of 10⁻⁶ -10⁻³ S/cm^{24, 28, 29}. Similar low conductivity was found in the three 2.5 PPV copolymers investigated in this study, as discussed in the results in Section 3.1. To improve the specific conductivity of the 2.5 PPV copolymers, a three-fold approach was taken: 1) increase the conjugation length of the hard block, 2) incorporate electron rich molecules into the hard block, and 3) employ blends of the 2.5 PPV copolymers with compatible, high conductivity materials. Steps 1 and 2 were accomplished by producing additional copolymers (Figure 2) that were modeled on the 2.5 PPV scaffold: 1) ethoxy substituted 2.5 PPV-4OEt to increase the conjugation length and 2) fluorene substituted FPV to incorporate electron rich molecules. Step 3 consisted of blending the 2.5 PPV copolymers with the fully conjugated PPV derivative poly-(2-

methoxy-5-(2-ethyl-hexyloxy)phenylene vinylene) (MEH-PPV) and with single-walled carbon nanotubes (SWCNT) and blending the MEH-PPV with the SWCNT. The scope of this study was then expanded to include investigation of the TE properties of the additional compounds. This chapter describes the process for synthesizing the p-type copolymers and the n-type monomers (Section 2.1), the preparation of the blend of the 2.5 PPV copolymers with MEH-PPV and with SWCNT and the blend of MEH-PPV with SWCNT (Section 2.2), and the instrumentation used to assess electrical conductivity and demonstrate the Peltier effect of the materials (Section 2.3).

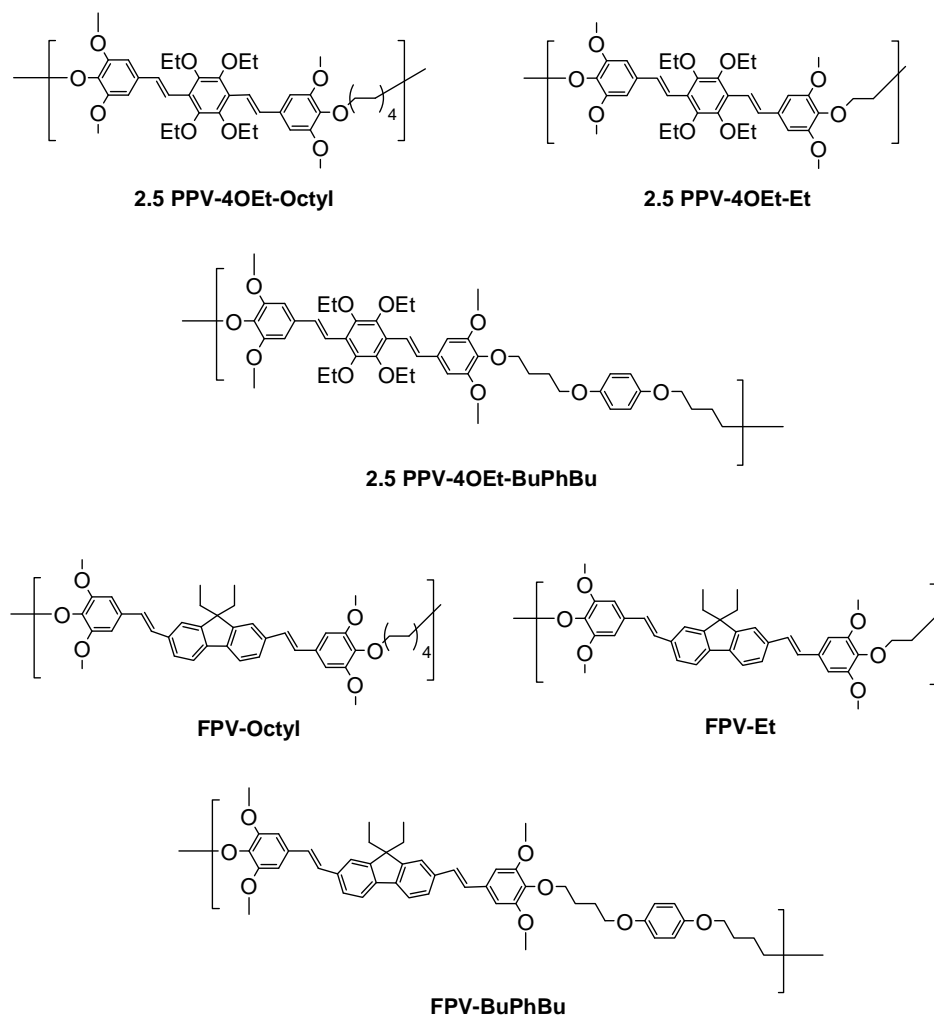


Figure 2. Ethoxy Substituted 2.5 PPV-4OEt and Fluorene Substituted FPV Copolymers Modeled on the 2.5 PPV-Octyl, -Et, and -BuPhBu Scaffold

2.1 Polymer Synthesis

2.1.1 *p*-Type Polymers

2.1.1.1 2.5 PPV. 2.5 PPV-Octyl was synthesized from the precursors: 1,2-bis-(2,6-dimethoxy-4-formylphenoxy)octane and α, α' -bis(tri-*n*-butyl phosphinyl)-*p*-xylene dibromide. 1,2-bis-(2,6-dimethoxy-4-formylphenoxy)octane was prepared by the reaction of 2,6-dimethoxy-

4-formylphenol with 1,8-dibromooctane. α, α' -bis(tri-*n*-butyl phosphinyl)-*p*-xylene dibromide was prepared by the reaction of α, α' -dibromo-*p*-xylene with tri-*n*-butyl phosphine.

2.5 PPV-Et was synthesized from the precursors: 1,2-bis-(2,6-dimethoxy-4-formylphenoxy)ethane and α, α' -bis(tri-*n*-butyl phosphinyl)-*p*-xylene dibromide. 1,2-bis-(2,6-dimethoxy-4-formylphenoxy)ethane was prepared by the reaction of 2,6-dimethoxy-4-formylphenol with 1,2-dibromomethane.

2.5 PPV-BuPhBu was synthesized from the precursors: 1,2-bis-(2,6-dimethoxy-4-formylphenoxy)-(1,4-bis-butoxy)benzene and α, α' -bis(tri-*n*-butyl phosphinyl)-*p*-xylene dibromide. 1,2-bis-(2,6-dimethoxy-4-formylphenoxy)-(1,4-bis-butoxy)benzene was prepared in two steps: 1) the reaction of hydroquinone with dibromobutane followed by 2) the reaction of 1,4-bis-(4-bromobutoxy) benzene with 2,6-dimethoxy-4-formylphenol.

Selected syntheses of the 2.5 PPV p-type polymers are shown in Figure 3.

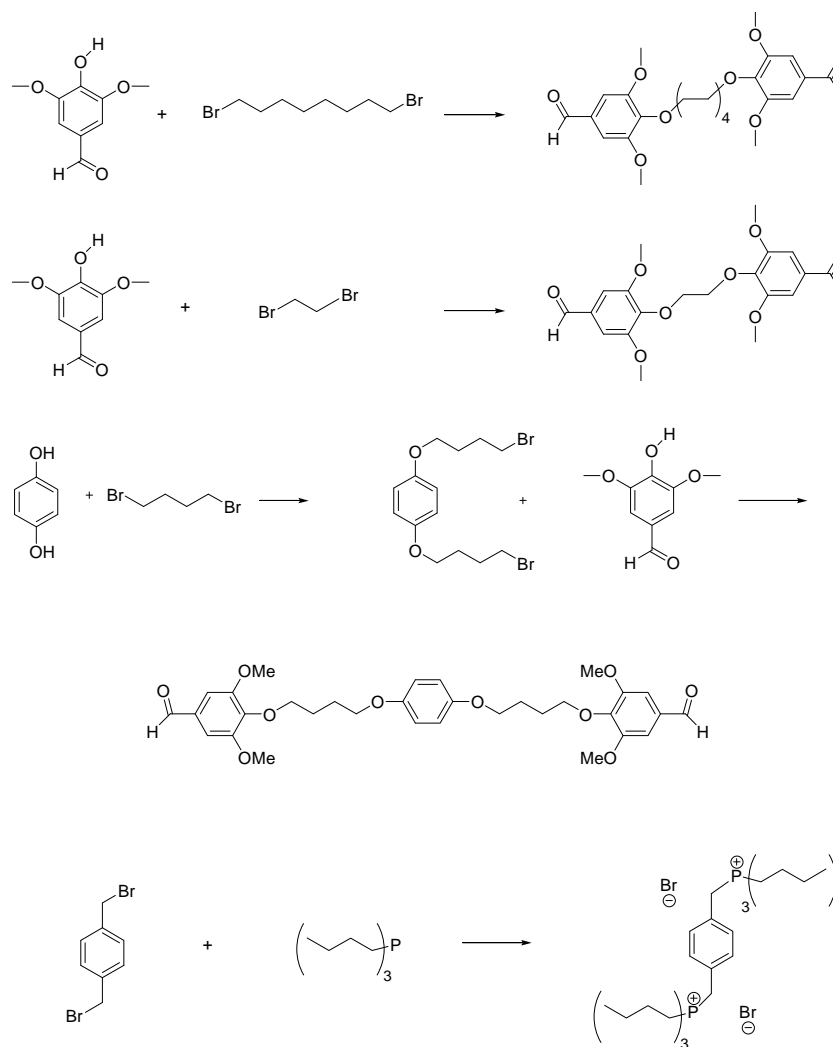


Figure 3. Synthesis of 2.5 PPV p-Type Polymers

2.1.1.2 2.5 PPV-4OEt. As shown in Figure 4, the 2.5 PPV-4OEt polymers were prepared by reaction of bis-aldehydes with α, α' -bis(tri-*n*-butyl phosphinyl)-*p*-(2,3,5,6-tetraethoxy)xylene dibromide, which was used in subsequent polymerization reactions with dialdehydes to afford the various 2.5 PPV-4OEt polymers. This compound was prepared in several steps. First, tetrahydroxy benzene was prepared by reducing 2,5-dihydroxyhydroquinone with tin metal in hydrochloric acid. This product was immediately reacted with ethylbromide under basic conditions to afford tetraethoxy benzene. Next, bis-bromomethyl tetraethoxy benzene was prepared by the reaction of bromomethylmethylether with tetraethoxy benzene under acidic conditions. This product was then immediately reacted with tri-*n*-butyl phosphine.

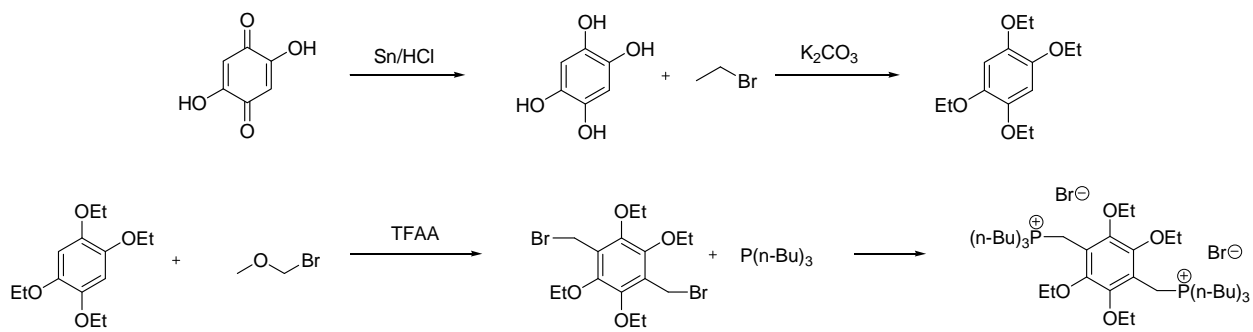


Figure 4. Synthesis of Reactant Used To Prepare 2.5 PPV-4OEt Polymers

2.1.1.3 Fluorene Phenylene Vinylenes (FPV). The FPV polymers were prepared by reaction of the aforementioned bis-aldehydes with α, α' -bis-2,7-(tri-*n*-butyl phosphinyl)-(9,9'-diethyl)fluorene dibromide, which was used in the subsequent polymerization reactions with various dialdehydes to afford the various FPV polymers. This compound was prepared in several steps (Figure 5). First, fluorene was reacted with two equivalents of bromoethane under basic conditions to afford 9,9'-diethyl fluorene, which was bromomethylated using paraformaldehyde and sodium bromide under acidic conditions to give 2,7-bis-bromomethyl-9,9'-diethyl fluorene. This compound was then treated with tri-*n*-butyl phosphine.

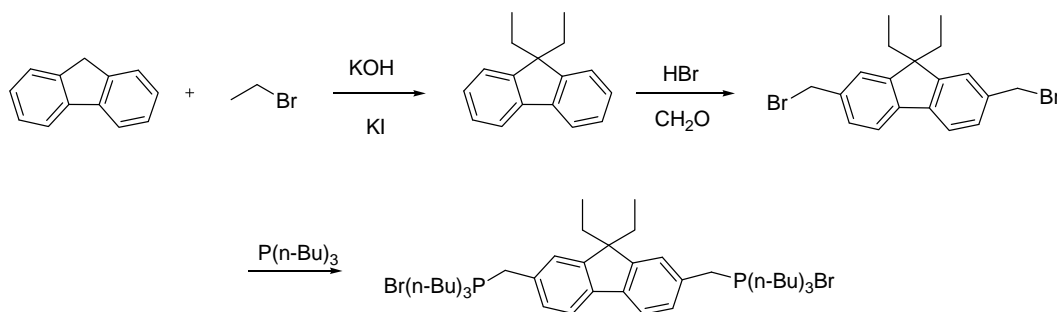


Figure 5. Synthesis of Reactant Used To Prepare FPV Polymers

2.1.2 n-Type Molecules and Polymers

Using the same flexible blocks as in the 2.5 PPV copolymers, the team attempted to prepare the corresponding bis-pyridinium derived n-type monomer. These experiments yielded only hemi-acetal derivatives, which could not be used for the subsequent polymerization reaction. To circumvent this problem, the conjugated portion of the molecule was first synthesized and then reacted with several dibromo compounds to provide electron deficient polymers, as shown in Figure 6. As an alternative to using n-type polymeric systems, the commercially available salt TTF-TCNQ was also used.

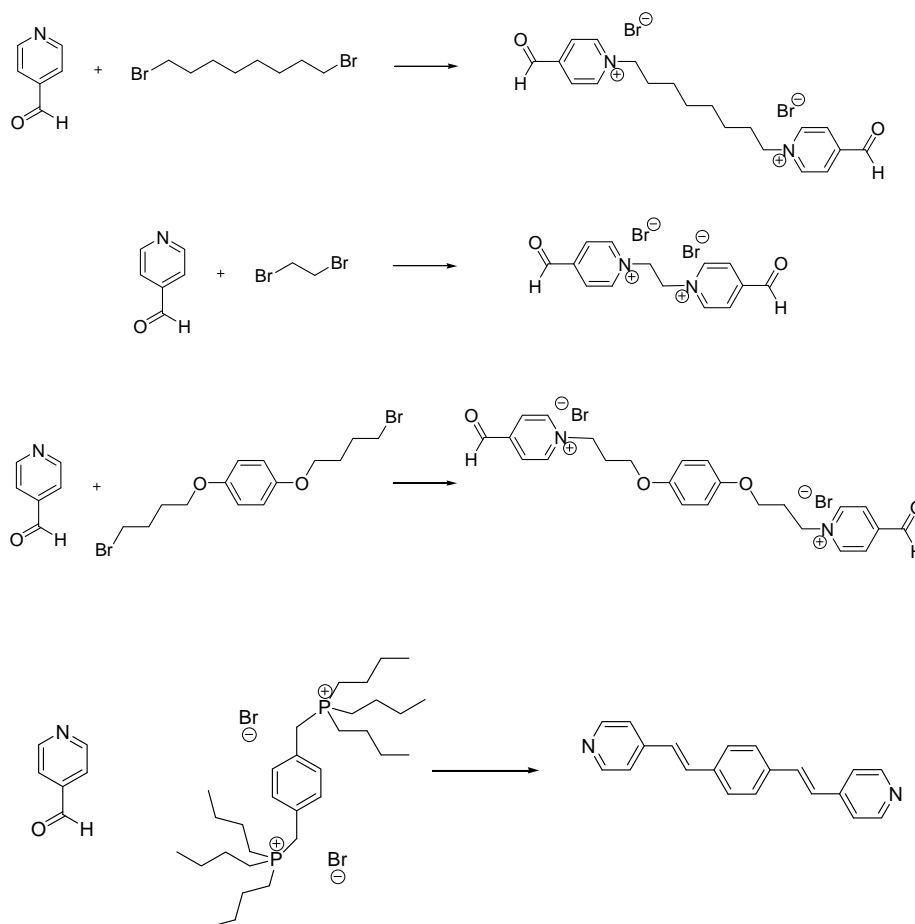


Figure 6. Synthesis of Reactants for n-Type Polymers

2.2 Blending with High-Conductivity Materials

Blends of the 2.5 PPV copolymers with various ratios of MEH-PPV were prepared by dissolving both polymers in a minimum amount of chloroform. The solutions were stirred 2-4 h before drop casting onto patterned Teflon plates and allowed to slowly evaporate and air dry for 12 to 24 h. The films were further dried under vacuum for 4 h and then stored under ambient conditions in the dark. Both the SWCNT blends with the 2.5 PPV copolymers and with MEH-PPV were prepared in a similar fashion as the 2.5 PPV/MEH-PPV blends except the solutions

were allowed to stir 12-15 h before film casting. This was to allow for adequate mixing of the SWCNT in the host polymer. Typical film dimensions were 2.5 cm x 0.4 cm x (50-600 μm).

2.3 Instrumentation To Assess Electrical Conductivity and To Demonstrate Peltier Effect

To investigate the electrical conductivity and TE properties of the materials of interest, instrumentation was constructed to provide reliable and reproducible measurements. To prevent noise from outside electrical sources the entire apparatus was enclosed in an aluminum frame which was grounded. Platinum wire was used for the source and probe contact material for the four-wire conductivity measurements and to determine Seebeck voltages. To ensure good contact between the probes and the sample, the platinum wire was embedded in a Teflon block, pressed firmly onto the sample, and held in place with two clamps. A Keithley 2440 source meter was used for all conductivity measurements, as well as for the current source for demonstrating the Peltier effect, which is discussed in Section 3.5. All voltage measurements, which included the Seebeck and differential thermocouple voltages, were made using a Keithley 6182 nanovoltmeter. A thermal gradient across the sample was established using a cartridge heater placed inside one of the two copper blocks while the other block was held at ambient temperature. A digital dual-input thermometer with k-type thermocouples pressed onto the tops of the films was used to measure the thermal gradient across the sample. To avoid electrical interference the thermocouple ends were coated with a thin layer of poly(vinyl chloride) (PVC); this also allowed for accurate determination of the temperature difference where the TE voltage was measured. Differential thermocouples (T-type) were constructed using thin-gauge copper-constantan wire and placed on either end of the sample. The design and schematics of the constructed device and measurement parameters are shown in Figure 7.

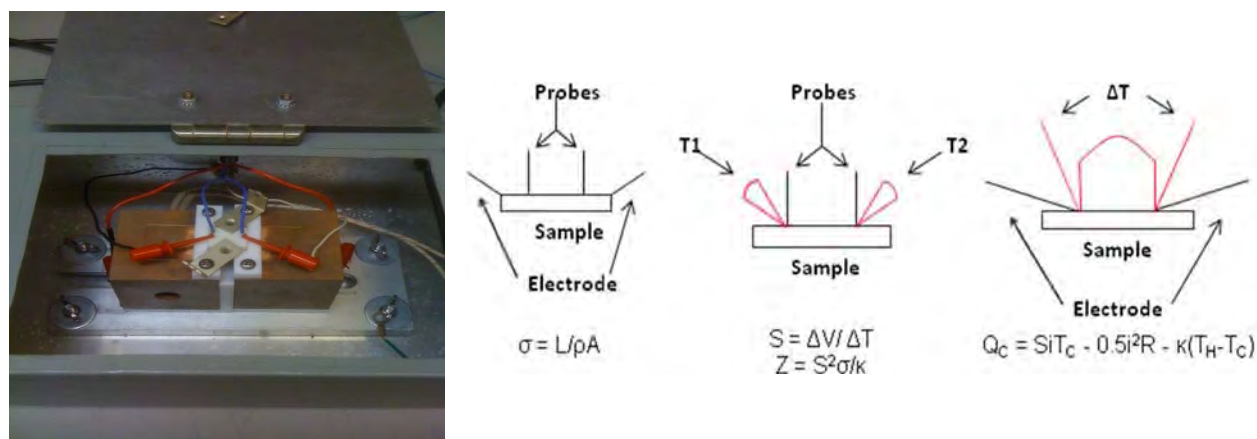


Figure 7. Device for Measurement of Electrical and TE Properties

The electrical conductivity of the samples was calculated from their corresponding I-V curves. The Seebeck coefficients were determined from the slope of the Seebeck voltage versus temperature difference plots. Demonstration of the Peltier effect in the samples was accomplished by passing a current through the sample and measuring the corresponding

temperature difference across the sample. Representative examples of these measurements are provided in Figure 8.

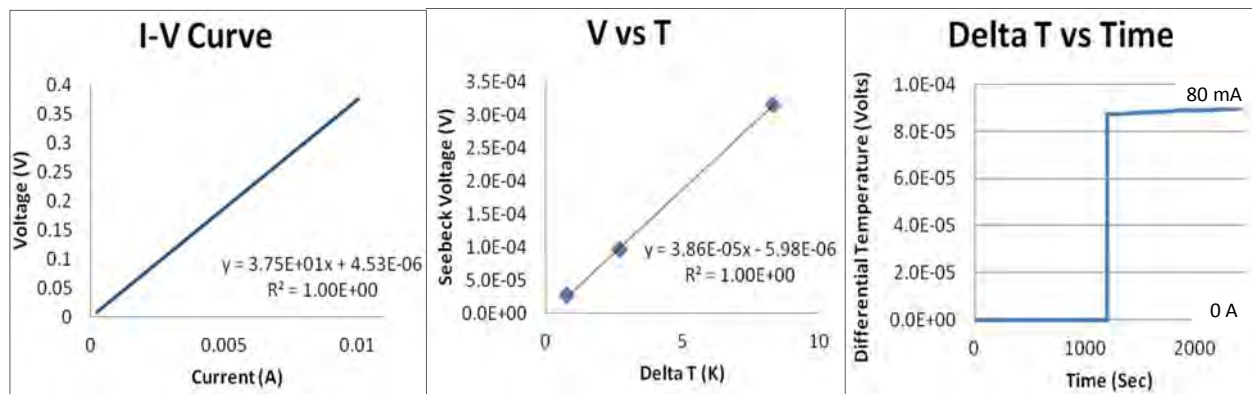


Figure 8. Representative Examples of σ , S , and ΔT Measurements (40% SWCNT in MEH-PPV)

3. RESULTS

3.1 2.5 PPV Copolymers

The conductivities of the 2.5 PPV copolymers were investigated for samples doped with p-TSA, iodine (I_2), and antimony pentafluoride (SbF_5) with various draw and doping ratios; the conductivity of the various samples is listed in Table 1. For samples with low conductivities, Seebeck voltages were difficult to measure due to Johnson noise associated with the high resistance of the films. To accurately determine the TE properties of the 2.5 PPV copolymers, multiple films were pressed together to reduce the sample resistance, which made it possible to accurately measure the Seebeck voltages. The results for various electrical and TE properties are shown in Table 2 for samples of the three copolymers doped with p-TSA and I_2 with different doping ratios and thicknesses.

Table 1. Electrical Conductivity of 2.5 PPV Copolymers (Single Films)

Polymer	Dopant	Draw Ratio	Conductivity (S/cm)
2.5 PPV-Octyl	p-TSA 1:1	1.0	1.172E-06
	p-TSA 1:1	2.2	5.056E-06
	p-TSA 1:2	1.0	2.759E-05
	p-TSA 1:2	3.9	8.197E-05
	I_2	4.85	2.969E-05
	SbF_5	1.0	8.904E-04
2.5 PPV-Ethyl	p-TSA 1:1	1.0	1.029E-06
	p-TSA 1:2	1.0	4.303E-05
	I_2	1.0	5.146E-06
	SbF_5	1.0	1.882E-04
2.5 PPV-BuPhBu	p-TSA 1:1	1.0	1.750E-06
	p-TSA 1:2	1.0	1.140E-04
	I_2	1	4.033E-04
	I_2	3.8	3.817E-05
	SbF_5	1.0	1.075E-03

As shown in Table 2, the 2.5 PPV copolymers exhibited high Seebeck coefficients, but due to their low electrical conductivities, showed only modest power factors and ZTs. In Table 2, and in the subsequent tables, the ZT of the 2.5 PPV copolymers and other systems were estimated using representative but conservative thermal conductivity values of $1.0 \text{ W/m}^2\text{K}$. Although the samples doped with SbF_5 showed the highest electrical conductivities, due to rapid de-doping/decomposition, the TE properties were transient. The effect of orientation on the copolymers' Seebeck coefficients will be investigated in future work.

Table 2. Electrical and TE Properties of 2.5 PPV Copolymers (Multi-Layer Films)

Polymer	Dopant	Thickness (cm)	Conductivity (S/cm)	Seebeck Coefficient ($\mu\text{V/K}$)	Power Factor ($\mu\text{W/m}^2\text{K}^2$)	ZT (@313K) ($\text{Kappa} = 1$)
2.5 PPV-Octyl	pTSA 1:1	3.10E-02	4.84E-05	2102.00	2.14E-02	6.69E-06
	pTSA 1:2	4.20E-02	4.21E-05	785.00	2.59E-03	8.12E-07
	I ₂	8.14E-02	4.65E-06	531.00	1.31E-04	4.10E-08
2.5 PPV-Ethyl	I ₂	1.66E-02	1.58E-02	115.60	2.11E-02	6.61E-06
	I ₂	1.66E-02	2.17E-02	-124.90	3.38E-02	1.06E-05
2.5 PPV-BuPhBu	p-TSA 1:2	2.15E-02	3.47E-04	2650.00	2.44E-01	7.64E-05
	I ₂	4.19E-02	5.35E-03	24.38	3.18E-04	9.95E-08

3.2 FPV and 2.5 PPV-4OEt Copolymers

Investigation of the electronic and TE properties of FPV-Et showed no improvement in conductivity and a decrease in Seebeck coefficient. The results for FPV-Et, which were expected to show the greatest improvement in the electrical conductivity due to the increased conjugation length, failed to produce significant increases in the electrical conductivity or TE performance. Hence the TE properties of the remaining FPV copolymers were not investigated during this project. The 2.5-PPV-4OEt copolymers proved to be unstable in air or for prolonged time in solution due to the substantial increase in electron density on the central phenyl ring. Attempts to form films of the 2.5-PPV-4OEt copolymers under a variety of conditions (solvent, atmosphere) proved unsuccessful and yielded brittle, brown films.

3.3. Blends

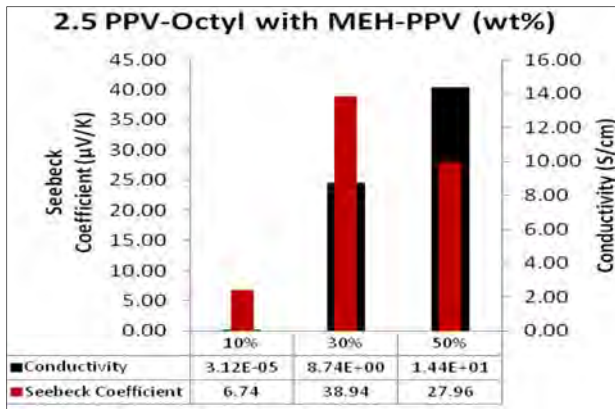
The electronic and TE properties of the 2.5 PPV copolymer blends were drastically improved with the addition of the highly conductive MEH-PPV and SWCNT materials, which were blended to improve the relatively low inherent conductivity of 2.5 PPV copolymers. The greatest improvement was achieved by blending the MEH-PPV and SWCNT, without the 2.5 PPV.

3.3.1 MEH-PPV with 2.5 PPV Copolymers

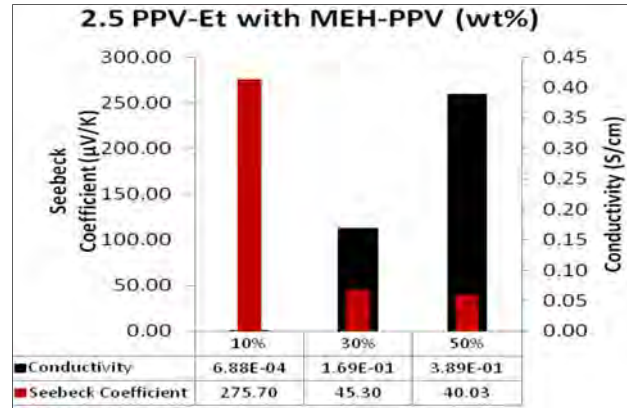
The results for different amounts of MEH-PPV blended with 2.5 PPV-Octyl, 2.5 PPV-Et, and 2.5 PPV-BuPhBu all doped with I₂, as well as 100% samples all doped with I₂ for each of the four polymers, are listed in Table 3. The Seebeck coefficients and conductivities for the blends only are compared in Figure 9. The blends showed substantial (four orders of magnitude) increases in their electrical conductivities and estimated figures of merit (two orders of magnitude). A non-linear decrease was observed in the Seebeck coefficients as the conductivity of the samples increased, showing it was possible to simultaneously increase the electrical conductivity and Seebeck coefficient in the blends.

Table 3. Electrical and TE Properties of Blends of MEH-PPV with 2.5 PPV Compared with 100% MEH-PPV and 100% 2.5 PPV Copolymers

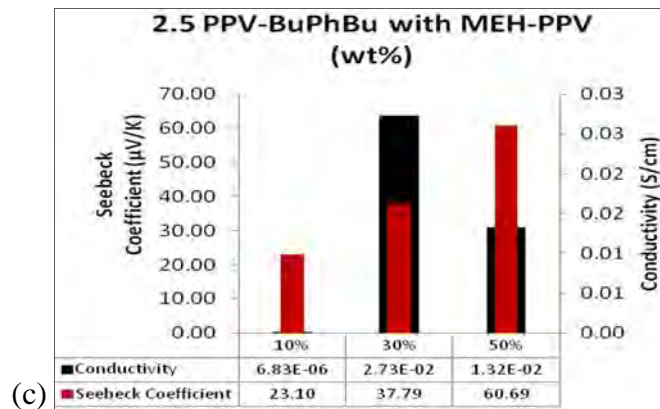
Polymer (% MEH-PPV)	Dopant	Thickness (cm)	Conductivity (S/cm)	Seebeck Coefficient ($\mu\text{V/K}$)	Power Factor ($\mu\text{W/m}^2\text{K}^2$)	ZT (@313K) (Kappa = 1)
100% MEH-PPV	I ₂	2.70E-03	2.31E-01	45.60	2.59E-02	7.77E-06
0%/2.5 PPV-Octyl	I ₂	8.14E-02	4.65E-06	531.00	1.31E-04	4.10E-08
10% in 2.5-Octyl	I ₂	1.10E-02	3.12E-05	6.74	1.42E-05	4.44E-08
30% in 2.5-Octyl	I ₂	2.30E-02	8.74E+00	38.94	1.33E+00	4.15E-04
50% in 2.5-Octyl	I ₂	2.21E-02	1.44E+01	27.96	1.12E+00	3.51E-04
0%/(2.5 PPV-Ethyl	I ₂	1.66E-02	1.58E-02	115.60	2.11E-02	6.61E-06
10% in 2.5-Ethyl	I ₂	6.71E-02	6.88E-04	275.70	5.23E-03	1.64E-06
30% in 2.5-Ethyl	I ₂	5.84E-02	1.69E-01	45.30	3.47E-02	1.09E-05
50% in 2.5-Ethyl	I ₂	1.92E-02	3.89E-01	40.03	6.23E-02	1.95E-05
0%/2.5 PPV-BuPhBu	I ₂	4.19E-02	5.35E-03	24.38	3.18E-04	9.95E-08
10% in 2.5-BuPhBu	I ₂	1.60E-02	6.83E-06	23.10	3.65E-05	1.09E-08
30% in 2.5-BuPhBu	I ₂	5.70E-02	2.73E-02	37.79	3.90E-03	1.22E-06
50% in 2.5-BuPhBu	I ₂	7.010E-02	1.32E-02	60.69	4.87E-03	1.52E-06



(a)



(b)



(c)

Figure 9. Seebeck Coefficient vs. Conductivity for 10%, 30%, and 50% Blends of MEH-PPV with 2.5 PPV: (a) 2.5 PPV-Octyl; (b) 2.5 PPV-Et; (c) 2.5 PPV-BuPhBu

3.3.2 SWCNT with 2.5 PPV Copolymers

The results for different amounts of SWCNT blended with 2.5 PPV-Octyl with different draw ratios and thicknesses both non-doped and doped with I₂ are listed in Table 4. The conductivity and Seebeck coefficient measurements for both the non-doped and I₂ doped 2.5 PPV-Octyl films at a draw ratio of 1 containing different percentages of SWCNT are compared in Figure 10. Compared to the neat 2.5 PPV-Octyl polymer films doped with I₂ (10⁻⁶ S/cm), a drastic increase was observed in the conductivity by incorporating SWCNT (10² S/cm). A decrease was observed in the Seebeck coefficient as the SWCNT content was increased, but the gain in electrical conductivity provided materials with figures of merit as high as 1x10⁻³, more than three orders of magnitude greater than the neat 2.5 PPV-Octyl films. Oriented films of the 2.5 PPV-Octyl systems containing 30% and 40% SWCNT showed only slight improvement in conductivity, Seebeck coefficient, and figure of merit.

Table 4. Electrical and TE Properties of Blends of SWCNT with 2.5 PPV-Octyl

Polymer (%SWCNT)	Dopant	Draw Ratio	Thickness (cm)	Resistance (Ω)	Conductivity (S/cm)	Seebeck Coefficient (μ V/K)	Power Factor (μ W/m ² K ²) _r	ZT (@313K) (Kappa = 1)
2% in 2.5-Octyl	I ₂	1	1.37E-02	7.97E+04	0.251	20.00	1.00E-02	3.14E-06
	I ₂	2.4	1.00E-02	5.24E+05	0.031	24.80	1.88E-03	5.88E-07
10% in 2.5 Octyl	None	1	7.10E-03	8.83E+04	0.197	57.80	6.57E-02	2.06E-05
	I ₂	1	1.00E-02	3.27E+03	2.677	17.62	8.31E-02	2.60E-05
	None	1.91	1.37E-02	4.34E+05	0.020	63.90	8.03E-03	2.51E-06
	I ₂	1.91	1.37E-02	1.32E+04	0.648	14.49	1.36E-02	4.26E-06
20% in 2.5 Octyl	None	1	1.11E-02	3.64E+04	0.356	47.80	8.14E-02	2.55E-05
	I ₂	1	1.110E-02	1.18E+03	10.973	16.20	2.88E-01	9.01E-05
	None	2.2	1.600E-02	3.10E+04	0.201	61.62	7.65E-02	2.39E-05
	I ₂	2.2	1.600E-02	2.09E+03	2.985	15.39	7.07E-02	2.21E-05
30% in 2.5 Octyl	None	1	0.0174	4.85E+03	1.091	52.87	3.05E-01	9.54E-05
	I ₂	1	0.0174	3.22E+02	16.415	15.73	4.06E-01	1.27E-04
	None	1.5	0.0112	1.34E+04	2.645	53.01	7.43E-01	2.33E-04
	I ₂	1.5	0.0112	1.13E+03	31.440	18.21	1.04E+00	3.26E-04
40% in 2.5 Octyl	None	1	0.0114	2.36E+03	5.210	44.80	1.05E+00	3.27E-04
	I ₂	1	0.0114	1.15E+02	106.914	12.90	1.78E+00	5.57E-04
	None	1.4	0.0106	6.36E+03	7.772	46.81	1.70E+00	5.33E-04
	I ₂	1.4	0.0106	4.32E+02	114.558	16.96	3.30E+00	1.03E-03

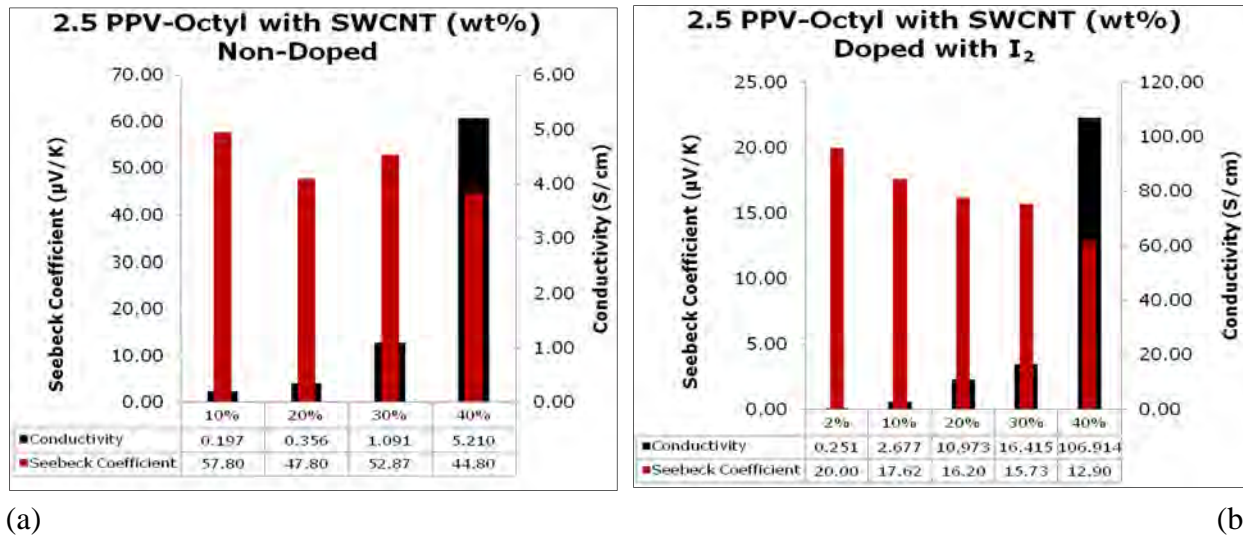
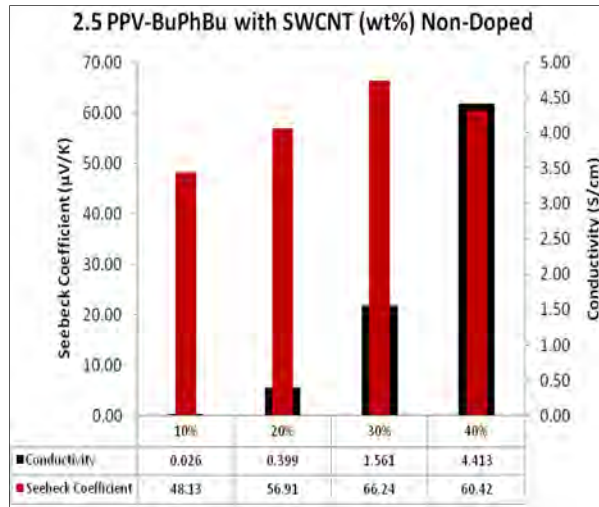


Figure 10. Seebeck Coefficient vs. Conductivity for 2%, 10%, 20%, 30%, and 40% Blends of SWCNT with 2.5 PPV-Octyl at Draw Ratio of 1: (a) Non-Doped; (b) Doped with I₂

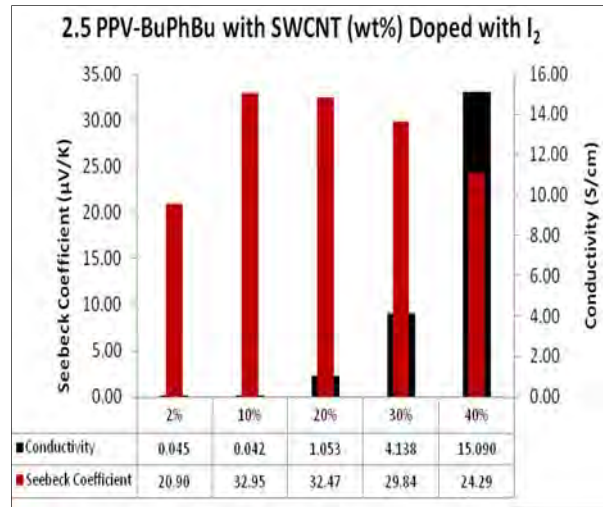
The results for different amounts of SWCNT blended with 2.5 PPV-BuPhBu both non-doped and doped with I₂ are listed in Table 5. The conductivity and Seebeck coefficient measurements for both the I₂ doped and non-doped blends of SWCNT with 2.5 PPV-BuPhBu are compared in Figure 11. The non-doped samples showed similar behavior as the 2.5 PPV-Octyl polymers blended with SWCNT; there was a significant increase (three orders of magnitude) in conductivity while the Seebeck coefficient remained constant. In the I₂ doped systems, a simultaneous increase was observed in both electrical conductivity and Seebeck coefficient up to 20% (wt) of SWCNT, after which the Seebeck coefficient showed very little change.

Table 5. Electrical and TE Properties of Blends of SWCNT with 2.5 PPV-BuPhBu

Polymer (%SWCNT)	Dopant	Thickness (cm)	Conductivity (S/cm)	Seebeck Coeff (μV/K)	Power Factor (μW/m ² K ²)	ZT (@313K) (Kappa = 1)
2% in 2.5 BuPhBu	I ₂	1.63E-02	4.52E-02	20.90	1.98E-03	6.18E-07
10% in 2.5 BuPhBu	None	1.79E-02	1.15E-02	56.30	3.65E-03	1.14E-06
	I ₂	2.04E-02	4.22E-02	32.95	4.58E-03	1.43E-06
20% in 2.5 BuPhBu	None	1.54E-02	2.42E-01	43.80	4.63E-02	1.45E-05
	I ₂	1.46E-02	1.05E+00	32.47	1.11E-01	3.48E-05
30% in 2.5 BuPhBu	None	1.69E-02	1.56E+00	66.24	6.85E-01	2.14E-04
	I ₂	1.69E-02	4.14E+00	29.84	3.68E-01	1.15E-04
40% in 2.5 BuPhBu	None	1.50E-02	4.41E+00	60.42	1.61E+00	5.04E-04
	I ₂	1.50E-02	1.51E+01	24.29	8.90E-01	2.79E-04



(a)



(b)

Figure 11. Seebeck Coefficient vs. Conductivity for 2%, 10%, 20%, 30%, and 40% Blends of SWCNT with 2.5 PPV-BuPhBu: (a) Non-Doped; (b) Doped with I₂

The results for different amounts of SWCNT blended with 2.5 PPV-Et both non-doped and doped with I₂ are listed in Table 6. The conductivity and Seebeck coefficient measurements for both the I₂ doped and non-doped blends of SWCNT with 2.5 PPV-Et are compared in Figure 12. As in the previous systems, the non-doped 2.5 PPV-Et composites showed very little change in Seebeck coefficient while the conductivity increased by four orders of magnitude (10^{-3} - 10^1 S/cm). In the samples doped with I₂ there was an initial drop in the Seebeck coefficient, but the conductivity increased by five orders of magnitude.

Table 6. Electrical and TE Properties of Blends of SWCNT with 2.5 PPV-Et

Polymer (%SWCNT)	Dopant	Thickness (cm)	Conductivity (S/cm)	Seebeck Coeff (μV/K)	Power Factor (μW/m ² K ²)	ZT (@313K) (Kappa = 1)
2% in 2.5 Et	I ₂	1.88E-02	2.33E-03	119.90	3.35E-03	1.05E-06
10% in 2.5 Et	None	9.80E-03	2.11E-01	63.30	8.46E-02	2.65E-05
	I ₂	9.80E-03	4.05E-01	17.20	1.20E-02	3.75E-06
20% in 2.5 Et	None	1.40E-02	8.68E-01	61.91	3.33E-01	1.04E-04
	I ₂	1.40E-02	2.48E+00	16.04	6.39E-02	2.00E-05
30% in 2.5 Et	None	1.24E-02	6.20E+00	66.09	2.71E+00	8.48E-04
	I ₂	1.24E-02	1.87E+01	13.50	3.40E-01	1.06E-04
40% in 2.5 Et	None	1.03E-02	9.69E+00	70.26	4.78E+00	1.50E-03
	I ₂	1.03E-02	2.79E+01	26.05	1.89E+00	5.92E-04

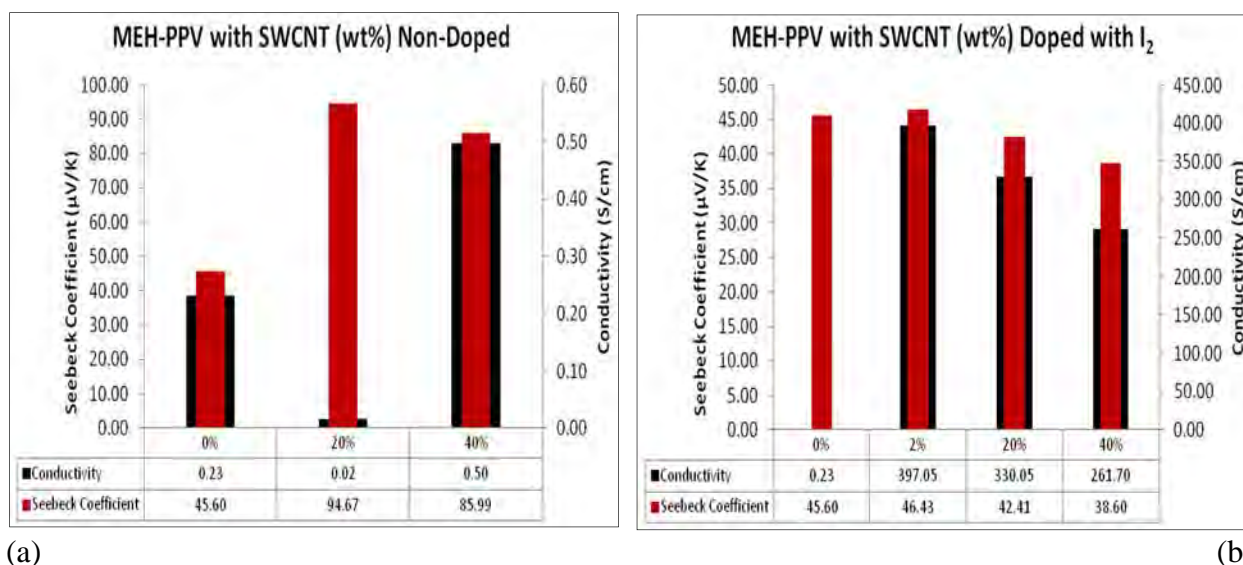


Figure 12. Seebeck Coefficient vs. Conductivity for 2%, 10%, 20%, 30%, and 40% Blends of SWCNT with 2.5 PPV-Et: (a) Non-Doped; (b) Doped with I₂

3.3.3 SWCNT with MEH-PPV

The blends of the fully conjugated PPV polymer MEH-PPV with SWCNT provided films with the highest conductivity while maintaining relatively unchanged Seebeck coefficients. The results for different amounts of SWCNT blended with MEH-PPV both non-doped and doped with I₂, as well as 100% MEH-PPV doped with I₂, are listed in Table 7. The conductivity and Seebeck coefficient measurements for both the I₂ doped and non-doped blends of SWCNT with MEH-PPV and the I₂ doped 100% MEH-PPV are compared in Figure 13. As in the previous systems, the non-doped MEH-PPV composites showed very little change in Seebeck coefficient while the conductivity was observed to increase by one order of magnitude (10^{-2} - 10^{-1} S/cm). In the samples doped with I₂ there was a drop in the Seebeck coefficient, but the conductivity increased by three orders of magnitude (10^{-1} - 10^2 S/cm) to yield samples with a ZT of approximately 0.03, among the higher values reported in the literature to date.

Table 7. Electrical and TE Properties of Blends of SWCNT with MEH-PPV and 100% MEH-PPV

Polymer (% SWCNT)	Dopant	Thickness (cm)	Conductivity (S/cm)	Seebeck Coeff (μV/K)	Power Factor (μW/m ² *K ²)	ZT (@313K) (Kappa = 1)
0% - PTP1097	I ₂	2.70E-03	0.23	45.60	2.59E-02	7.77E-06
2% - PTP2105	I ₂	3.50E-03	397.05	46.43	8.56E+01	2.68E-02
20% - PTP2106-1	None	5.90E-03	0.02	94.67	1.39E-02	4.36E-06
20% - PTP2106-2	I ₂	5.90E-03	330.05	42.41	5.94E+01	1.86E-02
40% - PTP2107-1	None	7.70E-03	0.50	85.99	3.69E-01	1.15E-04
40% - PTP2107-2	I ₂	7.70E-03	261.70	38.60	3.90E+01	1.22E-02

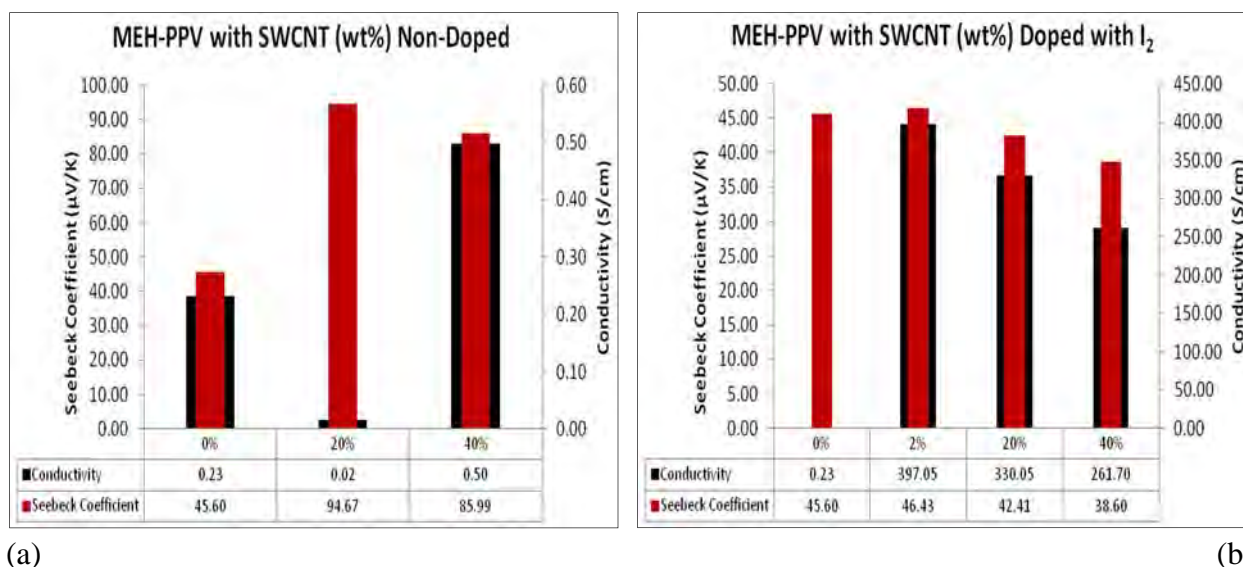


Figure 13. Seebeck Coefficient vs. Conductivity for 0%, 2%, 20%, and 40% Blends of SWCNT with MEH-PPV: (a) Non-Doped; (b) Doped with I_2

3.4 TTF-TCNQ

Compared to previously published work by Bubnova, et al,¹¹ who investigated TTF-TCNQ dispersed in insulating PVC, a two order of magnitude decrease was observed in the resistance (170 Ω vs. 11 k Ω) of the films by using the conjugated 2.5 PPV-Octyl copolymer while retaining a modest Seebeck coefficient of -40.6 $\mu\text{V}/^\circ\text{C}$ (Bubnova $S = -48 \mu\text{V}/^\circ\text{C}$). The power factor and estimated ZT for this material were found to be 3.47 $\mu\text{W}/\text{mK}^2$ and 1.09×10^{-3} , respectively. The significant increase in electrical conductivity may be attributed to an increase in electron mobility due to the conjugated block of the 2.5 PPV copolymer.

3.5 Demonstration of Peltier Effect

As described in Section 2.3, a suitable device was constructed to directly demonstrate the Peltier cooling effect in all of the systems investigated. To separate cooling in the sample due to the Peltier effect from the ubiquitous Joule heating, the temperature difference was recorded for the forward and reverse current directions (see Figure 14). The difference between the two temperatures was equal to two times the cooling produced in the sample. To limit the amount of Joule heating, the resistance of the samples needed to be minimized. Following the same strategy used for evaluation of the Seebeck coefficients of the 2.5 PPV copolymers, multiple films were stacked to provide thick films with sheet resistances 100 Ω or less. With the Joule heating minimized, a clear distinction in the heating and cooling cycles was readily observed upon reversing the current.

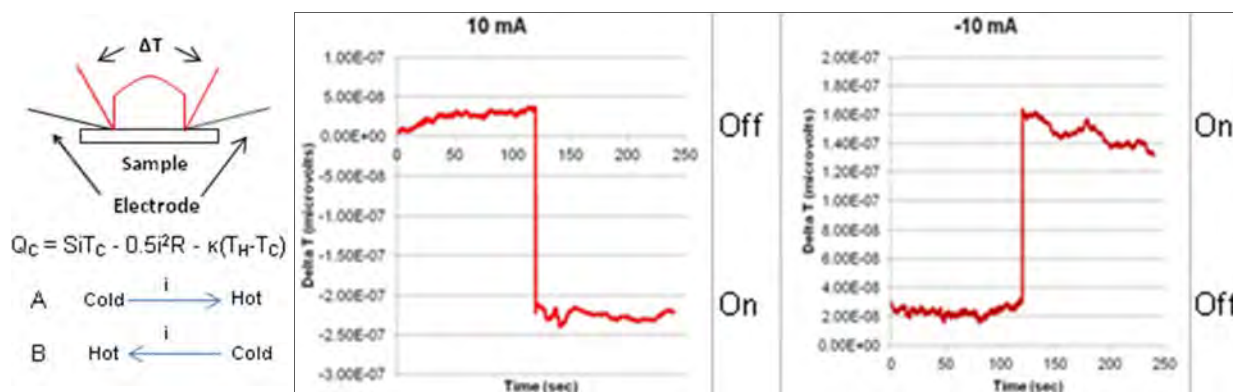


Figure 14. Schematic of Peltier Effect and Differential Temperature Voltages in 2.5 PPV-Octyl with SWCNT

Demonstration of the Peltier effect in the 2.5 PPV copolymers containing SWCNT was carried out for small currents at fixed voltages to avoid sample degradation. Due to the thickness of the films (higher resistance), Joule heating dominated the temperature changes in the samples. The maximum temperature gradient established in the samples was $\sim 0.1^\circ\text{C}$. The thicker films showed almost negligible Joule heating. The maximum temperature difference achieved was approximately 3°C in 2.5 PPV-Octyl containing 40% SWCNT. Due to the increase in conductivity and thermoelectric performance, the MEH-PPV films containing 40% SWCNT showed similar temperature differences in films with one-half to one-quarter the thickness. The absolute temperature differences observed were functions of the experimental conditions used.

4. CONCLUSIONS

The 2.5 PPV samples exhibited moderately large Seebeck coefficients, but due to the limited electrical conductivity the copolymer improvements in TE performance were less than expected. To improve the conductivity, copolymers with increased electron density (2.5 PPV-4OEt copolymers), increased conjugation length (FPV copolymers), and blended with highly conductive materials (MEH-PPV and SWCNT) were prepared, and their electronic and TE properties were investigated. The 2.5 PPV copolymer blends prepared with MEH-PPV and SWCNT showed drastic enhancement of the conductivity with only slight variations in the Seebeck coefficients as the amount of additive was increased. The resulting materials had estimated ZTs of 10^{-3} . Blends of the fully conjugated MEH-PPV with SWCNT were the most attractive materials studied due to their high electrical conductivities and essentially constant Seebeck coefficients. These blends had ZTs up to 10^{-2} , some of the highest observed for any organic TE materials in the literature to date.

The Peltier effect was successfully demonstrated in thin films of the most conductive samples, particularly the 2.5 PPV copolymers containing 40% SWCNT and the MEH-PPV blends with SWCNT, and were able to produce and maintain temperature gradients up to 3°C with non-optimized geometries. The n-type molecular composite, TTF-TCNQ in 2.5 PPV-Octyl, was investigated and found to have similar Seebeck coefficients but drastically improved electrical conductivity to a previous report. This material, in combination with the p-type systems already investigated, has been used to create, so far, a two-component thermopile.

Textile engineering based development of the materials produced in this research can result in a fabric demonstrating significant Peltier cooling. The processing versatility of TE organic polymers points to a spectrum of applications in which electrically powered cooling is required. Additionally, further materials development based on the results of the present study can be expected to yield second generation TE polymers with improved properties.

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